



P/1537-206

METHODS FOR THE REDUCTION AND CONTROL OF THE RELEASE  
OF GAS AND ODORS FROM SEWERAGE AND WASTE WATER

*CROSS-REFERENCE TO RELATED APPLICATIONS*

5 This application is a continuing application  
of pending U.S. Serial Number 08/386,735 filed February  
10, 1995. *has abandoned*

BACKGROUND OF THE INVENTION

*Field of the Invention*

10 The present invention relates to the control  
of gaseous release and of odors associated with  
sewerage and waste water and more particularly, to the  
reduction and control of the release of acid gases,  
such as hydrogen sulfide, from sewerage or waste water.

*Description of the Related Art*

15 Sewerage and waste water generally contain  
sulfates and other contaminants which, upon reduction,  
become (directly or indirectly) gaseous compounds which  
are released generating unpleasant odors. For example,  
sulfates are reduced to sulfides associated with the  
20 release of hydrogen sulfide gas. The reduction of  
sulfates can proceed by the action of sulfate-reducing  
bacteria including *Desulfovibrio sulfricans*. Hydrogen  
sulfide and other acid gases which are released include

potentially dangerous contaminants and lead to unpleasant odors.

Several methods have been proposed and used to control the release of hydrogen sulfide. These include methods which reduce the growth of the anaerobic bacteria or which chemically bind sulfides. However, these methods have drawbacks, such as high costs, implementation difficulties and safety concerns.

In particular, ferrous and ferric chloride (iron) and liquid caustic soda (sodium hydroxide, pH 13 - 14) are currently added to sewers to control sulfide generation and corrosion. The iron is added continuously to bind the sulfide as a nonsoluble iron sulfide precipitate.

Caustic soda is generally added semi-weekly to provide a thirty minute, high pH, shock dose to the anaerobic bacteria. The addition of caustic soda acts by neutralizing the sulfuric acid which has already been formed by the bacteria, inactivating and destroying the bacteria, and limiting the formation of new colonies of bacteria.

The use of caustic soda has been found to have several drawbacks. First, caustic soda only has a temporary effect on the bacteria. Second, caustic soda is hazardous and is highly toxic to humans. Even a small amount of caustic soda can cause permanent blindness.

It is expected that in the future the generation of hydrogen sulfide ( $H_2S$ ) will increase, particularly as more municipalities adopt water conservation programs that include the installation of low-flow plumbing devices. As a result of the reduced flows in such systems, water may be retained longer in the pipes, wet wells and force mains of the collection system; damming caused by settled solids and grease may increase; and less dissolved oxygen (DO) may be present due to increased biochemical oxygen demand (BOD). Absent the teachings of the present invention, all of these changes might otherwise exacerbate the problems addressed by the invention.

#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide methods which are safe and effective for controlling the formation and release of acid gases, particularly hydrogen sulfide.

It is also an object of the present invention to provide a method of maintaining a level of hydrogen sulfide which is below an acceptable level.

It is a further object of the invention to provide methods of reducing or eliminating odor associated with waste water or sewerage.

It is also an object of the present invention to provide a method to minimize the formation and release of both hydrogen sulfide and ammonia in waste water or sewerage.

5           It has been found that the formation and release of acid gases, particularly hydrogen sulfide, which are associated with the unpleasant odor of sewerage and waste water can be controlled or eliminated by introducing magnesium hydroxide and/or  
10           magnesium oxide into the contaminated water. Moreover, it has surprisingly been shown that magnesium hydroxide is able to maintain a pH level which minimizes the levels of both hydrogen sulfide and ammonia. Further, the levels of hydrogen sulfide and the pH of the  
15           contaminated water can be maintained at an acceptable level for a significant period of time.

          Other features and advantages of the present invention will become apparent from the following description of the invention which refers to the  
20           accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of illustrating the invention, there is shown in the drawings an embodiment which is presently preferred; it being understood,

however, that the invention is not limited by the precise arrangements and instrumentalities shown.

Figure 1 is graph of the relative concentrations of hydrogen sulfide and ionized hydrogen sulfide at various pH levels;

Figure 2 is a graph of the pH level and aqueous sulfide level after the addition of magnesium hydroxide; and

Figure 3 is a diagram of a representative configuration for the addition of magnesium hydroxide and/or oxide to waste water or sewerage.

#### DETAILED DESCRIPTION OF THE INVENTION

It has been found that the addition of an agent including magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ), and/or magnesium oxide ( $\text{MgO}$ ) to sewerage or waste water which is contaminated with compounds which can be reduced to acid gases, reduces or eliminates the release of these gases and the odor associated therewith.

The addition such an agent to sewerage or waste water is able to alter the pH of the solution into a preferred range of approximately 7.5 to 9.5, and to maintain pH in that preferred range for extended periods. The amount of the agent needed to achieve the preferred pH varies with the amount of water to be treated. Monitoring pH of the treated water during

addition of the agent is recommended so that the operator may increase or decrease the amount of agent as necessary.

5 In general, the fraction of hydrogen sulfide relative to ionized hydrogen sulfide which is present in solution is dependent on the pH of the solution. It is desirable to reduce the level of hydrogen sulfide which is not ionized so as to reduce the unpleasant and harmful odors associated therewith. As discussed in  
10 more detail below, applicants have discovered that a pH of 7.5-9.5 (especially 8.0-9.0) is particularly preferred both for reducing release of acid gas and also for maintaining better levels of other compounds as well.

15 As shown in Figure 1, which compares the ratio of hydrogen sulfide to ionized hydrogen sulfide, at a constant temperature, the percentage of ionized hydrogen sulfide increases with an increase in pH. The largest effect is seen in the pH range of 6.0 to 8.0.  
20 In particular, at a pH of 6.0, 90.1% is hydrogen sulfide, while at a pH of 8.0, only 8.3% is hydrogen sulfide. Further, at a pH of 8.5, 3% is hydrogen sulfide and at a pH of 9.0, the hydrogen sulfide level drops to less than 1%.

25 Therefore, due to the relative insolubility of the agent of the invention, conditions can be maintained over time in which the amount of hydrogen

sulfide which is present or released is reduced and therefore, the odors associated with the release or presence of hydrogen sulfide are minimized or eliminated. In some embodiments, hydrogen sulfide  
5 levels are desirably reduced to six parts per million or less.

Further, it has surprisingly been found that, at the preferred pH's of the invention, the undesirable release of ammonia is also minimized. In contrast to  
10 hydrogen sulfide levels, which decrease as the pH increases, the release of ammonia gas increases with an increase in pH. Therefore, a balance is preferred in which the pH level is both (1) high enough to reduce the formation and release of hydrogen sulfide and  
15 (2) low enough to prevent the formation and release of ammonia. It has been found that the optimal balance can be achieved by maintaining a pH in the range of approximately 7.5 to 9.5, especially 8.0 to 9.0, and most preferably, by maintaining a pH of approximately  
20 8.3.

Moreover, a pH level substantially above 9.0 can be harmful to bacteria which are beneficial to treatment of waste water and sewerage. In comparison to other pH increasing compounds, magnesium hydroxide  
25 has been found to slowly reach and maintain a pH in the desired range without substantially overshooting the

maximum level. As such, there is less osmotic shock and the helpful organisms are not destroyed.

Therefore, magnesium hydroxide and/or oxide have been found to be particularly suitable for the prevention of odor release in sewerage and waste water since the alkalinity and properties of magnesium hydroxide are such that it is easy for the operator to keep pH levels within the preferred range discussed above, without inadvertently raising pH so far above the preferred range that the undesirable effects discussed above become problematic.

Moreover, it has been found that the low solubility of the magnesium leads to a time released alkalinity so that the pH level is more stable and is maintained upstream for a longer period of time. As shown in Figure 2, magnesium hydroxide was able to maintain a pH of above 7.5 and a level of aqueous sulfides at or below 5 ppm for thirty days.

In addition to the benefits of magnesium hydroxide and/or oxide discussed above, the use of magnesium hydroxide and/or oxide is preferable for a number of reasons. First, it is noted that magnesium hydroxide requires no placarding or special handling and presents no chemical hazard to the environment, users, or the public. Second, magnesium hydroxide has a higher neutralizing capacity per mole than caustic soda due to its two OH ions. Third, the by-products



produced by the reaction of magnesium with hydrogen sulfide tend not to be hazardous as with some by-products of hydrogen sulfide reactions. Finally, the magnesium requirements are less dependent on sulfide concentration.

It is believed that two mechanisms are responsible for the effectiveness of magnesium hydroxide and/or magnesium oxide. First, magnesium hydroxide has a pH of approximately 10.5, which, while safe to humans, is above the tolerance of common acid producing bacteria. It is noted that small amounts of lime (calcium hydroxide) can be added to magnesium hydroxide and/or magnesium oxide slurry to increase the pH and enhance the slurry's ability to kill bacteria. It is anticipated that other biocides or hardening agents such as sodium silicate, sodium bi-sulfate, magnesium sulfate, magnesium chloride, phosphates, or other materials intended to impart mechanical strength, may be added to further enhance its performance.

Secondly, as the bacteria is re-established, the alkalinity provided by the magnesium hydroxide and/or magnesium oxide neutralizes the acids produced by the bacteria and prevents the rapid re-establishment of bacteria.

A magnesium hydroxide and/or magnesium oxide slurry can be prepared by adding caustic calcined magnesium oxide (MgO), preferably in a dry powder form,

to water. The magnesia can be obtained from any of the known suppliers including Premier Services Corporation, King of Prussia, Pa. Premier Services sells magnesia in dry powder form under the trademark MAGOX®.

5                   When magnesium oxide is added to water it undergoes hydration and is converted to magnesium hydroxide. The rate of this reaction can be varied depending upon the surface area of the MgO, starting water temperature, vessel configuration, and agitation.  
10                  Either a slowly hydrating MgO, or a fully hydrated Mg(OH)<sub>2</sub> slurry may be added to the contaminated water.

                  A magnesium hydroxide slurry can also be purchased from any of the known suppliers, including Premier Services which sells a magnesium hydroxide  
15                  slurry under the trademark AQUAMAG®.

                  In a preferred embodiment of the invention, a specially hydrated and formulated slurry, marketed by Premier Services Corporation under the trademark THIOGUARD™, is added to sewerage or waste water.  
20                  Without intending to be broad by theory, it is believed that this slurry offers a safe, economic alternative reagent for acid neutralization and water treatment and has been found to be particularly effective in controlling odors inter alia by achieving the pH and  
25                  other effects discussed herein. It is believed to neutralize harmful sulfuric acid. It is an off-white slurry composed predominately of agglomerated magnesium

hydroxide particles and is made from hydrated calcined natural magnesite or precipitated from sea water, bitterns, or brines. Table I, below, sets forth a representative chemical analysis of it on a loss free basis.

**TABLE I**

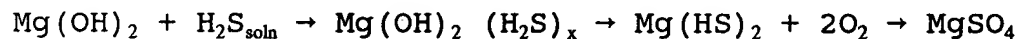
Viscosity, centipoise	800-6000, typically 3000
% Solids	55-65
Specific Surface Area	Typically 10 m <sup>2</sup> g <sup>-1</sup>
Chemical Analysis (Dry Basis), wt%	
MgO	90-99
CaO	0.3-4.0
SiO <sub>2</sub>	0.3-4.0
R <sub>2</sub> O <sub>3</sub>	0.1-2.0

The component R<sub>2</sub>O<sub>3</sub> refers to natural impurities such as Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> which are indigenous to ore bodies. Other insolubles besides (or in addition to) SiO<sub>2</sub>, e.g. MgCO<sub>3</sub> and/or CaCO<sub>3</sub> may be included. The product THIOGUARD™ is made from natural ore and there are some natural variations in the percentages of various ingredients as shown inter alia in Table I.

In a preferred embodiment, as shown in Figure 3, the magnesium hydroxide or magnesium oxide in the form of a slurry is topically applied to a stream of sewerage or waste water. In particular, a storage tank or drum 1 which holds magnesium hydroxide and/or magnesium oxide pumps the magnesium through a maintenance hole 2 to a sewerage flow 3. Odors from downstream maintenance holes 4 and corrosion on crowns and maintenance holes 5 are reduced or eliminated.

Addition of sufficient THIIOGUARD™ to the sewerage to raise the pH to 9.0 - 9.5, which takes somewhere between 8.5 - 100 mg/l, dependent upon type of sewerage is sufficient to reduce odor and corrosion problems in sanitary sewers. This occurs because at this pH dissolved hydrogen sulphide gas is at a minimum and does not tend to escape into gaseous phase and contribute to odor and corrosion. For instance addition of THIIOGUARD™ to sewerage at approximately 100 mg/l results in an almost instantaneous drop of aqueous sulphides from an initial 16 ppm to less than 1.0 ppm for a period of 4 days and a subsequent rise to between 6-6.5 for a period of 50 days.

Apart from its ability to alter sewerage pH to reduce dissolved hydrogen sulphide gas, there is a surface reaction between THIIOGUARD™ and dissolved hydrogen sulphide, which results in adsorption of the gas onto the solids phase.



Further reaction results in the formation of magnesium hydrosulphide, which can be oxidized by dissolved oxygen to form soluble magnesium sulphate which does not substantially contribute to odor or corrosion.

Due to its limited solubility in water, it is very slow to release hydroxyl ion (OH<sup>-</sup>) in normal pH range of sewerage compared to other alkalis such as lime and caustic soda.



Consequently, THIIOGUARD™ is able to continue to raise the pH downstream of the original point of addition without resulting in excessively high local pH's. For instance, adding it at a rate of 100 mg/l to sewerage

is capable of sustaining a pH greater than 8.5 for 24 hours.

5 Its use to control odor/corrosion problems in sewerage is not limited to just hydrogen sulphide but could encompass other acidic gases/vapors such as sulphur dioxide and sulphur compounds which contain an ionizable hydrogen ion, such as mercaptans containing the -SH group.

10 It should be realized by those skilled in the art that the magnesium hydroxide and/or magnesium oxide can be added to any other water or liquid solution that is contaminated by compounds which can be reduced to acid gases, particularly sulfates and mercaptans.

15 The characteristics of the magnesium hydroxide and/or magnesium oxide slurry can be varied to provide the optimum pumping characteristics and to treat different levels of contamination.

20 The properties of the slurry can be varied by any of the known methods including changes in the solids to water ratio, or by the use of polymers to enhance or alter these properties as desired for differing field conditions or equipment configurations, e.g., increasing or decreasing the water content or by adding in more magnesia powder.

25 It is recommended that the slurry should include at least 30%, preferably at least 50%, by weight magnesium compound in the form of magnesium oxide, magnesium hydroxide or a mixture thereof.

30 Magnesium oxide can also be mixed with sodium silicate to produce a slurry which, when dried, yields a hard alkaline material composite of unhydrated magnesium oxide encapsulated in sodium silicate. In some embodiments, this dry form may constitute the agent added to sewerage or waste water in accordance with the invention. The acid produced by surface  
35 bacteria is neutralized by the sodium silicate. In

addition, as the sodium silicate dissolves, the magnesium oxide is exposed, thereby dehydrating the bacteria and neutralizing the hydrogen sulfide.

5           Although the present invention has been  
described in relation to particular embodiments  
thereof, many other variations and modifications and  
other uses will become apparent to those skilled in the  
art. It is preferred, therefore, that the present  
invention be limited not by the specific disclosure  
10           herein, but only by the appended claims.